

# Copolymerization of Carbon Monoxide and Styrene with the Nd(III)–Cu(II) Catalyst

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**ABSTRACT:** In this article, the linear alternating copolymer of carbon monoxide and styrene was obtained using the Nd(III)–Cu(II) catalyst. It was found that the introducing order of the catalyst components can affect the catalytic activity, and the pre-prepared catalyst had higher catalytic activity than the *in situ* catalyst. The promoting effect of copper acetate on the catalytic activity was also investigated. The structure of the copolymer was characterized by means of IR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , WXR, and EA methods. The thermal decomposition properties were checked by the way of TGA. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 8–13, 2001

**Key words:** neodymium acetate; carbon monoxide; styrene; alternating copolymerization

## INTRODUCTION

The alternating copolymer of ethylene and CO has attracted considerable interest from both academia and industry over the last decades.<sup>1</sup> The main reasons are as follow: first, carbon monoxide is relatively inexpensive. Second, polymers containing polyketones have the potential to become photodegradable or biodegradable polymers in a new class. Third, the carbonyl group can be easily modified chemically. The copolymerization reaction mechanism has been extensively discussed by several scientists, such as Drent,<sup>1,2</sup> Brookhart,<sup>3,4</sup> Vrieze,<sup>5</sup> Sen,<sup>6</sup> and Consiglio.<sup>7</sup> The industrial interest in these new materials is witnessed by the early announcement by Shell of the incoming commercial availability of Carilon, a CO/ethylene/propylene polyketone.<sup>8</sup> For the copolymerization of CO and styrene, there has been an increasing number of reports appearing in the current literature. Palladium is the most often used catalyst. Although the catalytic activity is

relatively higher, but the catalytic activity center palladium(II) could be reduced to Pd<sup>(0)</sup>. For complexes bearing nitrogen ligands, the Pd<sup>(0)</sup> may immediately lose its ligand and precipitate as metallic palladium. That will result in a decrease of the thermostability of the obtained polyketone and increase of the production costs because the effective utilization ratio of palladium reduced.

To develop new cheaper catalyst systems, in the present work rare earth salt was used as a catalyst in the copolymerization of CO and styrene. The structure of the copolymer was determined from IR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ . The effects of preparation methods of the catalyst on the catalytic activity and the promoting effect of the cocatalyst cupric acetate were discussed.

## EXPERIMENTAL

### Materials

Carbon monoxide (>99.9%) was supplied by Dalian Science and Engineering University. Methanol was dried by anhydrous MgSO<sub>4</sub> and then distilled. Styrene was purified by CaH<sub>2</sub> drying and vacuum distillation. Neodymium oxide

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was supplied by the Baotou Rare Earth Research Institute and ignited before used. All other chemicals were purchased from Huabei Special Chemical Co. and directly used without purification.

### Anhydrous Neodymium Acetate Synthesis

Four grams ignited neodymium oxide was refluxed with 200 mL of acetic anhydride. A light blue suspension was formed that turned violet in color upon applying heat. The suspension cleared when the refluxing became vigorous; the rare earth compound settled to the bottom of the flask as a viscous mass, which quickly formed a hard cake. After 2 h of refluxing, the solid mass was broken up thoroughly, and refluxing continued for 4–8 h. The product was recovered by filtration, washing, and drying. Products after drying were found to give analytical results demonstrating that the anhydrous acetates had been formed. Found C, 22.19; H, 2.98; Nd, 44.9. calc. For Nd(OAc)<sub>3</sub>; C, 22.42; H, 2.82; Nd 44.89%.

### Copolymerization of CO and Styrene

The alternating copolymerization of CO and styrene was conducted in a 100 mL autoclave according to the general procedure of ref. 9. Typically,  $3 \times 10^{-4}$  mol neodymium acetate,  $1.48 \times 10^{-4}$  mol cupric acetate,  $6.2 \times 10^{-4}$  mol 1,10-phenanthroline,  $8.6 \times 10^{-4}$  mol *p*-toluenesulfonic acid, and  $1.0 \times 10^{-3}$  mol *p*-benzoquinone were dissolved in 5 mL methanol and 15 mL styrene. The mixture was placed in the reactor and charged with 5 MPa of CO, heated to the desired temperature (60°C). After the given time, the reaction stopped by cooling to room temperature and venting the unreacted CO.

The product, in the form of a white, fine powder, was recovered by precipitation with methanol and hydrochloric acid, filtrated, and washed several times with methanol and water, then dried in vacuum. Anal. Found: C, 80.84%; H, 6.02%; O, 13.14%; Calcd. for the alternating copolymer of CO and styrene: C, 81.82%; H, 6.06%; O, 12.12%.

### Measurements

Thermogravimetric analysis was performed on a Dupont thermal analysis system model TA2000 under nitrogen at heating rates of 10°C/min. The infrared spectrum was done by using the potassium bromide pellet technique with Nicolet 5DX-FTIR spectrometry. The <sup>1</sup>H-NMR spectrum was run with a Bruker NMR spectrometer, model AC-P200. Solid-state <sup>13</sup>C-NMR was measured by a Bruker NMR spectrometer, model MSL 200MHz. The chemical shifts were referenced to internal tetramethylsilane (TMS). Wide-angle X-ray diffraction (WXR) investigation of the copolymer were carried out on powder samples with an Ital-structures  $\theta/\theta$  diffractometer equipped with a thermostatic control system using nickel-filtered CuK<sub>α</sub> radiation. The scan wide was 2–50°, and step length was 0.02°.

## RESULTS AND DISCUSSION

The copolymer of CO and styrene using rare earth as a catalyst was almost insoluble in common solvents, and its alternative structure was characterized by IR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR spectroscopy and supported by elemental analysis.

**Table I** IR Analysis Result of CO/Styrene Copolymer Using Different Catalysts

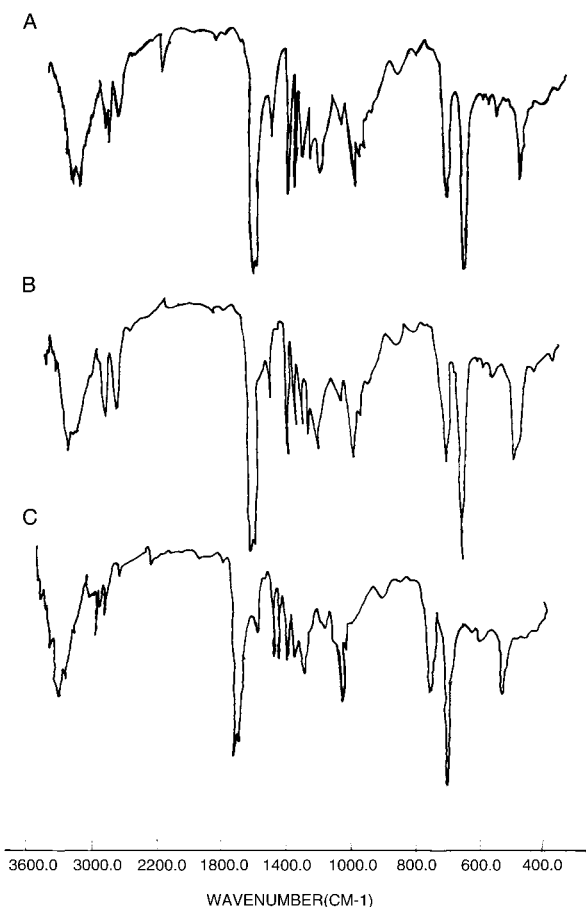
Catalyst	$\nu_{\text{C=O}}$ (cm <sup>-1</sup> )	$\nu_{\text{=CH}}$ (cm <sup>-1</sup> )	$[\eta]$ (mL/g)
Nd(CH <sub>3</sub> COO) <sub>3</sub> <sup>a</sup>	1707, 1695	698, 748	13.20
Cu(CH <sub>3</sub> COO) <sub>2</sub> <sup>b</sup>	1708, 1697	698, 750	8.95
Nd(CH <sub>3</sub> COO) <sub>3</sub> —Cu(CH <sub>3</sub> COO) <sub>2</sub> <sup>c</sup>	1709, 1697	698, 751	14.21
Pd(CH <sub>3</sub> COO) <sub>2</sub> <sup>d</sup>	1709	696, 748	15.60

<sup>a</sup> Nd(CH<sub>3</sub>COO)<sub>3</sub>  $3.0 \times 10^{-4}$  mol, mol ratio of 1,10-phenanthroline/Nd(III) = 2, *p*-toluenesulfonic acid/Nd(III) = 3, *p*-benzoquinone/Nd(III) = 3, methanol 5 mL, styrene 15 mL, 60°C, 5 Mpa, 6 h.

<sup>b</sup> Cu(CH<sub>3</sub>COO)<sub>2</sub>  $1.0 \times 10^{-3}$  mol, mol ratio of 1,10-phenanthroline/Cu(II) = 5, *p*-toluenesulfonic acid/Cu(II) = 6, *p*-benzoquinone/Cu(II) = 10, methanol 5 mL, styrene 15 mL, 60°C, 5 Mpa, 6 h.

<sup>c</sup> Nd(CH<sub>3</sub>COO)<sub>3</sub>  $3.0 \times 10^{-4}$  mol, Cu(CH<sub>3</sub>COO)<sub>2</sub>  $1.0 \times 10^{-4}$  mol, other conditions were same as <sup>a</sup>.

<sup>d</sup> Palladium acetate  $1.05 \times 10^{-4}$  mol, mol ratio of 2,2'-bipyridine/Pd(II) = 8, *p*-toluenesulfonic acid/Pd(II) = 6, *p*-benzoquinone/Pd(II) = 55, methanol 5 mL, styrene 15 mL, 60°C, 4.0 Mpa, 2 h.



**Figure 1** FTIR spectra of the copolymer of CO and styrene. (A) Catalyzed by neodymium acetate; (B) catalyzed by cupric acetate; (C) catalyzed by the Nd(III)–Cu(II) system.

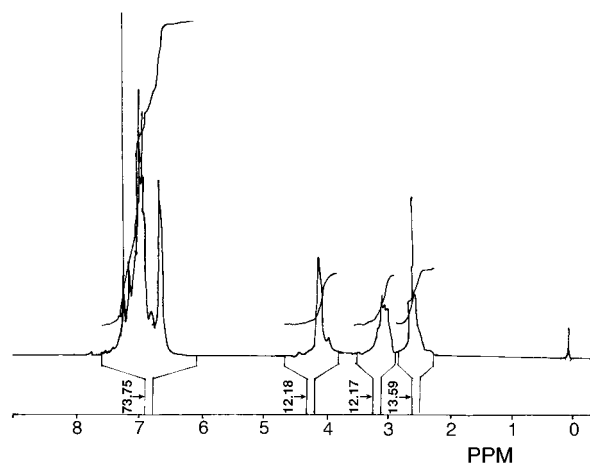
### IR Analysis of CO/styrene Copolymer

Table I summarizes the IR analysis results of the CO/styrene copolymer respectively prepared in the presence of cupric acetate (A), neodymium acetate (B), and neodymium acetate-cupric acetate (C).

The Infrared spectrum of all the copolymers in Figure 1 include two at  $1709$  and  $1697\text{ cm}^{-1}$  that are attributed to carbonyl groups in the copolymer.

### Characterization of CO/styrene Copolymer Prepared in the Presence of a Nd(III)–Cu(II) Catalyst by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$

The  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectrogram of CO/styrene copolymer by a Nd(III)–Cu(II) catalyst are shown in Figure 2 [7.4–6.5 (5H, m), 3.8–4.2 (1H, br), 2.9 (1H,s), 2.4 (1H,s)] and Figure 3. Both of them appear to be consistent with that of per-

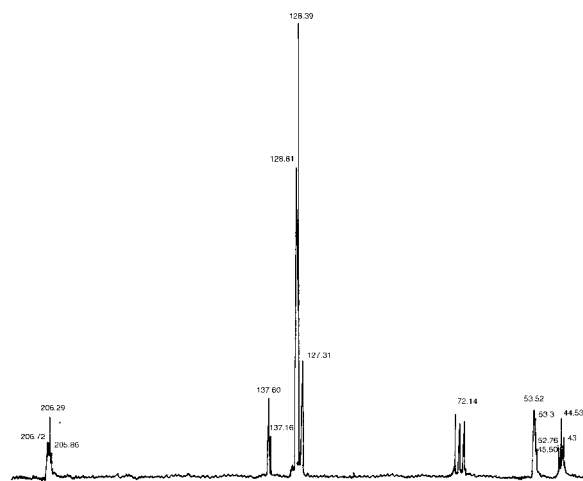


**Figure 2**  $^{13}\text{C-NMR}$  spectrum of the ST/CO copolymer obtained using the Nd–Cu catalyst.

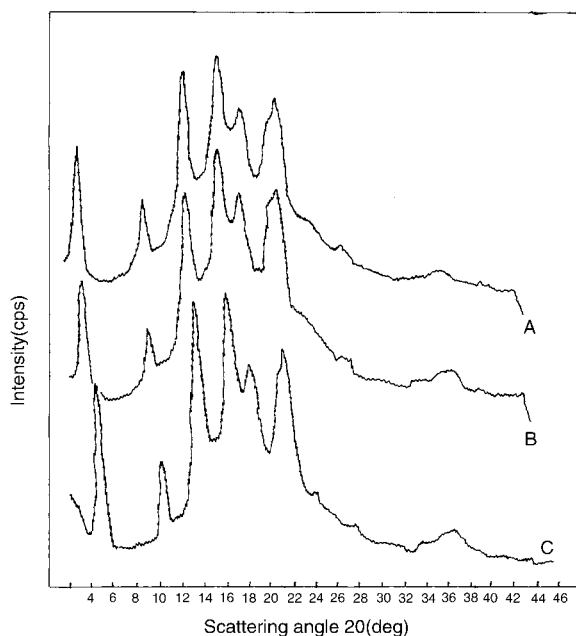
fect alternating polyketones from styrene and carbon monoxide and extremely similar to CO/styrene copolymer obtained with a palladium catalyst.<sup>10</sup> The resonances at 44.53, 53.52, and 206.29 ppm in the  $^{13}\text{C-NMR}$  spectrum are assigned to backbone methylene, methyne, and carbonyl carbons, respectively, of the repeating molecular unit  $-\text{CH}_2\text{CHPhCO}-$ . The aromatic carbon resonances are located at 127.31, 128.39, 129.51, and 137.60 ppm. Thus, the NMR analysis confirms chemoselectivity to a perfectly alternating copolymer of carbon monoxide and styrene.

### X-ray Diffraction Diagram

Figure 4 shows the X-ray diffraction diagrams of the CO/styrene copolymer by the Nd(III)–Cu(II)



**Figure 3**  $^{13}\text{C-NMR}$  spectrum of the ST/CO copolymer obtained using the Nd–Cu catalyst.

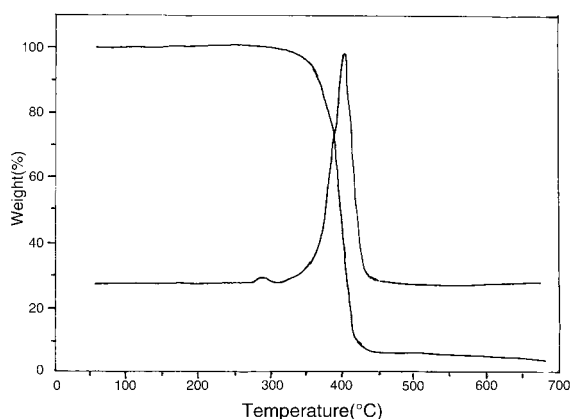


**Figure 4** WAXD patterns of of the copolymer of CO and styrene. (A) Catalyzed by neodymium acetate; (B) catalyzed by cupric acetate; (C) catalyzed by the Nd(II)-Cu(II) system.

catalyst. It displays many sharp lines indicative of a fairly high degree of crystallinity. The shape of X-ray diffraction diagram of this copolymer is very similar to that of the copolymer, which is copolymerized by a palladium catalyst.<sup>10</sup>

### Thermogravimetric Analysis

A TGA curve of the CO/styrene copolymer by rare earth catalyst appears in Figure 5 with a heating rate  $20^{\circ}\text{C min}^{-1}$  in nitrogen. As can be seen, the



**Figure 5** TGA and its drivative curve of the CO/styrene copolymer by the Nd-Cu catalyst in nitrogen.

**Table II** Effect of Cupric Acetate on the Copolymerization of CO and Styrene<sup>a</sup>

Neodymium Acetate (mol)	Cupric Acetate (mol)	R( $10^2$ g CP <sup>b</sup> /mol Nd · h)
$3 \times 10^{-4}$	0	1.0
$2 \times 10^{-4}$	0	1.3
$3 \times 10^{-4}$	$1 \times 10^{-4}$	2.8
$2 \times 10^{-4}$	$1 \times 10^{-4}$	3.3

<sup>a</sup> Molar ratios: 1,10-phenanthroline/Nd(III) = 2, *p*-toluenesulfonic acid/Nd(III) = 3, *p*-benzoquinone/Nd(III) = 3, methanol 5 mL, styrene 15 mL,  $60^{\circ}\text{C}$ , 5 Mpa, 6 h.

<sup>b</sup> CP is the alternating copolymer of carbon monoxide and styrene.

loss of mass starts at  $380.14^{\circ}\text{C}$ . The maximum decomposition occurs at  $402.24^{\circ}\text{C}$  according to the differential thermogravimetric analysis curve, the same as the CO/styrene copolymer from a palladium catalyst.<sup>10</sup>

The CO/styrene copolymer from the Nd(III)-Cu(II) catalyst was insoluble in common organic solvents, but is soluble in *m*-cresol and hexafluoro-*i*-propanol. From the above analysis results it demonstrates that this copolymer has a similar structure with that from the palladium catalyst. Both are perfectly alternating copolymers and have higher crystallinity. But it has a lower melting point  $\sim 274^{\circ}\text{C}$  than that from the palladium catalyst ( $\sim 289^{\circ}\text{C}$ ).

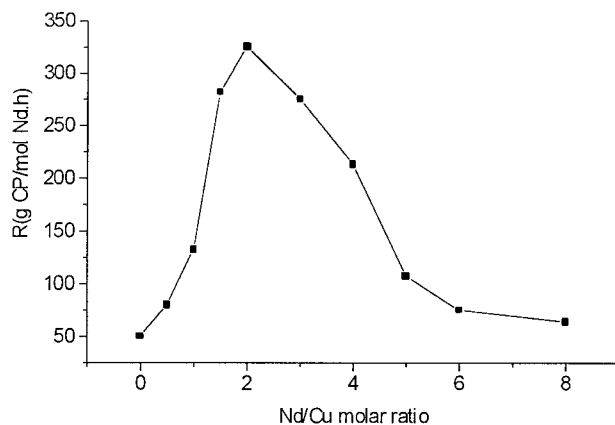
### Promoting Effect of Cupric Acetate

As we have demonstrated, the CO/styrene copolymer can be obtained in the presence of the catalyst system composed of neodymium acetate, 1,10-phenanthroline, *p*-toluenesulfonic acid, and *p*-benzoquinone. It was also found that the addition of cupric acetate to the above catalyst system can improve the catalytic activity of Nd(III) sig-

**Table III** Copolymerization of Styrene and CO Using Cupric Acetate as Catalyst

Cu(CH <sub>3</sub> COO) <sub>2</sub> (mol)	R( $10^2$ g CP/mol Nd · h)
$0.5 \times 10^{-4}$	0
$1 \times 10^{-4}$	0
$5 \times 10^{-4}$	0.09
$10 \times 10^{-4}$	0.21

<sup>a</sup> Molar ratios: 1,10-phenanthroline/Cu(II) = 5, *p*-toluenesulfonic acid/Cu(II) = 6, *p*-benzoquinone/Cu(II) = 10, methanol 5 mL, styrene 15 mL,  $60^{\circ}\text{C}$ , 5 Mpa, 6 h.



**Figure 6** Effect of the Nd/Cu molar ratio on the copolymerization. \*R is the catalytic activity of the Nd constant over three polymerization times. Cupric acetate  $1.48 \times 10^{-4}$  mol, 1,10-phenanthroline/Nd(III) = 2 (mol ratio), *p*-toluenesulfonic acid/Nd(III) (mol ratio) = 2, *p*-benzoquinone/Nd(III) (mol ratio) = 3, methanol 5 mL, styrene 15 mL, 60°C, 5 Mpa, 6 h.

nificantly. The results of the addition of Cu(II) to affect the catalytic activity of Nd(III) for the copolymerization of styrene and carbon monoxide at 60°C are shown in Table II.

To compare the catalytic effect of Cu(II) with Nd(III), Table III shows the results of the polymerization of styrene and carbon monoxide only with cupric acetate as the catalyst.

Table III shows that trace copolymer can be obtained only when the dosage of Cu(II) is large enough. So Cu(II) can be used as a cocatalyst of Nd(III), as shown in Table III. When  $1.48 \times 10^{-4}$  mol cupric acetate was added to  $3.25 \times 10^{-4}$  mol neodymium acetate, a catalytic activity of 400 g CP/mol Nd · h was obtained for the copolymerization of styrene and CO.

### Effect of the Nd/Cu Molar Ratio on Copolymerization Reaction

The effect of the Nd/Cu molar ratio on the copolymerization of CO with styrene is shown in Figure 6. It can be seen from Figure 6 that the Nd/Cu molar ratio has a strong effect on the catalytic activity of neodymium. The highest productivity can be achieved when the Nd/Cu molar ratio is about 2.0. The lower value of the Nd/Cu molar ratio leads to a lower amount of the catalytic active center. On the other hand, if too much neodymium acetate was added to the copolymerization system, the excess neodymium acetate could not be used effectively because of the lower solubility of it in the reaction system.

### Effect of Introducing Order of Catalyst Component

The introducing order of the catalyst components plays an important role in the activity of the catalyst system. From Table IV, the relatively higher activity of the catalyst was observed using method 4, and the lower activity using method 5. *p*-Benzoquinone has a stronger coordination ability to Nd(III) than *p*-toluenesulfonic acid. If *p*-benzoquinone was introduced to the reaction system before *p*-toluenesulfonic acid, the stable complex of benzoquinone with Nd(III) will be formed and the active centers would be occupied, resulting in the decreasing of the catalytic activity of Nd(III). On the other hand, early introducing of the weaker coordinating *p*-toluenesulfonic acid was advantageous to the interaction of Nd(III) and the monomers.

### Copolymerization of Carbon Monoxide and Styrene by Presynthesized Nd(III)–Cu(II) Catalyst

Several Pd(II) systems, either prepared *in situ* or involving presynthesized complexes, have been

**Table IV** Effect of the Introducing Order of the Catalyst Components on the Catalytic Activity<sup>a</sup>

No.	Introducing Order	$[\eta]$ (mL/g)	R(10 <sup>2</sup> g CP/mol Nd · h)
1	Nd + Cu + phen <sup>b</sup> → + methanol → PTSA + PQ	10.97	2.80
2	Nd + Cu + phen + PTSA <sup>c</sup> → + methanol → + PQ	15.23	3.13
3	Nd + Cu + phen + PTSA + PQ <sup>d</sup> → + methanol	11.05	2.87
4	Nd + Cu + PTSA → + methanol → + phen + PQ	14.21	3.47
5	Nd + Cu + PQ → + methanol → + phen + PTSA	12.35	2.08
6	Nd + Cu + PTSA + PQ → + methanol → + phen	14.37	2.71

<sup>a</sup> Reaction conditions: Nd  $3.2 \times 10^{-4}$  mol, Cu  $1.0 \times 10^{-4}$  mol, phen  $6.0 \times 10^{-4}$  mol, PTSA  $9.3 \times 10^{-4}$  mol, PQ  $1 \times 10^{-3}$  mol, methanol 5 mL, styrene 15 mL, CO 5 MPa, 60°C, 6 h.

<sup>b</sup> 1,10-Phenanthroline.

<sup>c</sup> PTSA-*p*-toluenesulfonic acid.

<sup>d</sup> PQ-*p*-benzoquinone.

**Table V Copolymerization of Styrene and CO with the Presynthesized Catalysts**

No.	Presynthesizing Method	R(10 <sup>2</sup> g CP/mol Nd · h)
1.	All the catalyst components were dissolved in methanol, the catalyst precursor was obtained by volatilizing the solvent under the room temperature.	3.47
2.	Neodymium acetate, cupric acetate, and <i>p</i> -toluenesulfonic acid were dissolved in ethyl cyanide, then <i>p</i> -benzoquinone and 1,10-phenanthroline were added in order, after stirring, the blue powder was obtained through filtrating, washing, and drying.	3.54
3.	The catalyst was prepared <i>in situ</i> .	2.7

\* Reaction conditions: neodymium acetate  $3.0 \times 10^{-4}$  mol, cupric acetate  $1.1 \times 10^{-4}$  mol, 1,10-phenanthroline  $5.8 \times 10^{-4}$  mol, *p*-toluenesulfonic acid  $8.6 \times 10^{-4}$  mol, *p*-benzoquinone  $1.0 \times 10^{-3}$  mol, methanol 5 ml, styrene 15 ml, CO 5 MPa, 60°C, 6 hr.

reported to homogeneously catalyze the copolymerization of CO and olefins. In general, the presynthesized catalyst was found to have lower productivity than the comparable in such system.<sup>11,12</sup> Here, we prepared the Nd(III)–Cu(II) catalyst precursors by two ways, and their catalytic activities were given in Table V.

From Table V, it can be seen that the catalyst precursors have higher catalytic activities than the corresponding *in situ* catalyst.

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